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Spectroscopic Determination of the
A.C. Voltammetric Response

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January 6, 1984

SPECTROSCOPIC DETERMINATION

OF THE

A.C. VOLTAMMETRIC RESPONSE

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ABSTRACT

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INTRODUCTION

The electrochemical literature of the past decade reveals an increasing interest in the spectroscopic monitoring of electrode reactions[1]. Although a large number of spectroscopic methods have been utilized to advantage, UV-visible absorption spectroscopy has been the most extensively exploited. One of the most important advantages of measuring the change in absorbance resulting from an electrode reaction, as opposed to measurement of the resulting current, is the additional selectivity afforded by including wavelength as an experimental variable.

UV-visible absorption spectroelectrochemistry as carried out either at optically transparent electrodes (OTE's)[2] or in reflectance experiments at conventional solid planar electrodes[3-8] has been used to great advantage in the spectroscopic characterization of primary and secondary products of electrode reactions, and in mechanistic studies of homogeneous reactions coupled to an electrode reaction (see, for example, references (4-8)). Recently, Bancroft et al.[9] have extended chronocoulometric theory to spectroscopic observation at OTE's to yield a method for the determination of heterogeneous charge transfer parameters. These authors note that the additional selectivity afforded by spectroscopic determination of the electrochemical response is particularly advantageous when dealing with solvents or redox species which are difficult to purify. No readily implementable spectroelectro-

chemical method, however, has been previously discussed which provides quantitative information about the charge transfer process while retaining qualitative mechanistic information of the type which has made cyclic voltammetry[10] such a popular tool for the study of electrode reactions.

Alternating current techniques[11] have long been recognized as methods of choice for the quantitative characterization of electrode processes. More recently, with the advent of linear sweep cyclic AC voltammetry[12, 13], it has been shown that AC methods can retain at least as much, and often more, qualitative diagnostic information as the more popular technique of cyclic voltammetry.

When an alternating current results from alternate formation and removal of one form of a redox couple at the surface of an electrode surface, the intensity of a beam of light either transmitted through or reflected from the surface of the electrode will vary in accordance with the alternation of the relative concentrations of the two forms of the redox couple, provided that they have different molar absorptivities at the wavelength of the radiation. This alternation of light intensity has already been exploited in the technique of modulated specular reflectance spectroscopy (MSRS)[3-8]. Here, a typically large amplitude periodic square wave potential is applied to the electrode such that first one and then the other form of a redox couple predominate periodically at the surface of an electrode. A phase sensitive detector (PSD) is used to monitor the variation in

intensity of a light beam reflected from the surface of the electrode and the PSD output plotted vs. wavelength provides a difference spectrum of the oxidized and reduced forms of the electroactive species. Although this technique has been used to provide qualitative support for proposed reaction mechanisms at surfaces[3] and in the diffusion layer[4-8], no example of its use in a quantitative manner exists.

We show here that if a small amplitude sinusoidal perturbation is superimposed on a slowly varying cyclic potential ramp applied to an electrode, the output of a PSD monitoring a light beam reflected from the electrode surface mirrors the charging current corrected AC voltammetric response. Sinusoidally modulated AC reflectance spectroscopy (SMACRS) is implemented with the same instrumentation[7] as previously used in MSRS and retains both the qualitative and quantitative utility of linear sweep AC voltammetry in conjunction with the advantages of spectroscopic observation.

THEORY AND PRACTICAL CONSIDERATIONS

As mentioned above, UV-vis absorption spectroelectrochemistry can be carried out by measurement of the intensity of a light beam either transmitted through or reflected from an electrode. Although what follows is equally applicable, in principle, to OTE's, the reflectance experiment has several important advantages. First, the intensity of a light beam transmitted through an OTE may be considerably

reduced relative to that reflected from the corresponding solid electrode.
Second, OTE's formed by deposition of a thin conducting film on a
transparent substrate often have high resistances which may not be
compensated for by positioning the Luggin capillary close to the
electrode surface and can lead to uneven current distribution across
the electrode surface. Third, because in the reflectance experiment
the light beam passes through the double layer twice at some angle
from a normal to the electrode surface, it encounters a greater
number of the species of interest. The reflectance technique is thus
inherently more sensitive. Fourth, since the secondary electrode
must not obstruct the light path, it is not possible in a transmission
experiment to arrange the working electrode such that all points on
its surface are equidistant from the counter electrode. The resulting
potential distribution across the electrode surface may be particularly
undesirable when working in non-aqueous electrolyte solutions or
at optically transparent thin layer electrodes. For these reasons we
confine our discussion to measurement of the AC response by
reflectance spectroscopy.

Winograd et al. have shown[14] that for the electrode process with
no homogeneous complications

$$Ox + ne^- \rightleftharpoons Red$$
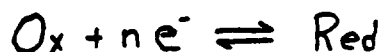
the absorbance-time profile measured at an OTE at a wavelength where
only the reduced species absorbs is given by

$$A(t) = \frac{\epsilon_R}{n \mathcal{F} A} \int_0^t i(t)\, dt \qquad (1)$$

where $\mathcal{A}(t)$ is the absorbance, ϵ_R is the molar extinction coefficient of the reduced species, and other notation is conventional. If both the oxidized and reduced forms of the electroactive species absorb at the wavelength of the incident radiation, then

$$\mathcal{A}(t) = \frac{\Delta\epsilon}{n\mathcal{F}A} \int_0^t i(t)\, dt \qquad (2)$$

where $\Delta\epsilon = \epsilon_R - \epsilon_{ox}$ is the difference in molar absorptivities of the two forms of the redox couple. Where the light beam has been reflected from the electrode surface, this result must be corrected for the fact that the light passes through the double layer twice. Inclusion of the correction factor as previously discussed for MSRS[3] leads to

$$\mathcal{A}(t) = \frac{2\Delta\epsilon}{n\mathcal{F}A\cos\theta} \int_0^t i(t)\, dt \qquad (3)$$

where θ is the angle between the incident radiation and a perpendicular to the electrode surface. When single beam spectrometers are used in reflectance experiments the parameter generally measured is

$$\frac{\Delta R}{R} = \frac{R(t) - R_0}{R_0} \qquad (4)$$

where $R(t)$ is the intensity of the reflected light beam at some time t and R_0 is its intensity at $t=0$. Since $\frac{R(t)}{R_0} = 1 - \frac{\Delta R}{R}$, and from Beer's law $\mathcal{A}(t) = \log\frac{R_0}{R(t)}$, it follows that

$$-\ln\left(1+\frac{\Delta R}{R}\right) = 2.303\, \mathcal{A}(t) \qquad (5)$$

Substituting (5) into (3) gives

$$-\ln\left(1+\frac{\Delta R}{R}\right) = \frac{4.606\,\Delta\epsilon}{n\mathcal{F}A\cos\theta} \int_0^t i(t)\, dt \qquad (6)$$

This result is quite general provided no homogeneous complications exist, and the derivation of the spectroscopic response to a potential perturbation is thus simply a matter of performing the appropriate integration. When $\frac{\Delta \mathcal{R}}{\mathcal{R}}$ is small, as is most often the case, (6) can be further simplified to

$$- \frac{\Delta \mathcal{R}}{\mathcal{R}} = \frac{4.606 \; \Delta \epsilon}{n \; \mathcal{F} A \cos \theta} \int_o^t i(t) \, dt \qquad (7)$$

As given by Smith[11], for a simple quasi-reversible electrode process, $O_x + n e^- \rightleftharpoons Red$, the fundamental harmonic current resulting from the superposition of a small amplitude potential perturbation, ΔE , on some DC bias potential, E_{DC} , is

$$I(\omega t) = I_{rev} \; F(t) \; G(\omega) \; \sin(\omega t + \phi) \qquad (8)$$

where

$$I_{rev} = \frac{n^2 \mathcal{F}^2 A \; C_{ox}^{bulk} (\omega \, D_{ox})^{\frac{1}{2}} \; \Delta E}{4 \, R T \, \cosh^2(j/2)} \qquad (9)$$

is the amplitude of the current expected for a perfectly reversible electrode process,

$$F(t) = (1 + e^{-j})(\alpha \, C_{ox} + (D_R / D_{ox})^{\frac{1}{2}} \beta \, e^{j} \, C_R) / C_{ox}^{bulk} \qquad (10)$$

and

$$G(\omega) = 2 / \left[1 + (1 + \frac{(2\omega)^{\frac{1}{2}}}{\lambda})^2 \right] \qquad (11)$$

take into account the effects of non-Nernstian behaviour in the DC and AC time scales respectively, and

$$\phi = \cot^{-1}(1 + \frac{(2\omega)^{\frac{1}{2}}}{\lambda}) \qquad (12)$$

with

$$\lambda = k_s \left(e^{-\alpha \dot{f}} + e^{\beta \dot{f}} \right) / D^{1/2} \qquad (13)$$

$$\dot{f} = n \mathcal{F} (E_{DC} - E_R^{\ddagger}) / RT \qquad (14)$$

and

$$D = D_{OX}^{\beta} \, D_R^{\alpha} . \qquad (15)$$

gives the phase angle between the applied sinusoidal voltage and the resulting fundamental harmonic current. All other notation has its usual meaning.

The fundamental harmonic alternating component of the concurrent specular reflectance response, as detectable either by tuned amplification or phase sensitive detection, is given by substituting (8) into (7) to give

$$-\mathcal{R}(\omega t) = \frac{4.606 \, \Delta \epsilon}{n \mathcal{F} A \cos \theta} \, I_{rev} \, F(t) \, G(\omega) \int_0^t \sin(\omega t + \phi) \, dt \qquad (16)$$

where, for simplicity, we have defined the normalized parameter $\mathcal{R}(\omega t) = \frac{\Delta \mathcal{R}}{\mathcal{R}}(\omega t)$. It is important to note that the function $F(t)$, which expresses a time dependence of the amplitude of the sinusoidal current, remains constant with respect to the AC time scale under the slow scan rate restriction[11, 13] (i.e. $2\pi \nu \ll \omega \Delta E$, where ν is the linear scan rate) common to AC voltammetric methods, and hence does not enter into the integration. Carrying out the integration and cancelling terms gives

$$-\mathcal{R}(\omega t) = \mathcal{R}_{rev}\, F(t)\, G(\omega)\, \cos(\omega t + \phi) \qquad (17)$$

where
$$\mathcal{R}_{rev.} = \frac{4.606\, \Delta E\, n\, \mathcal{F}\, \Delta E\, C_{ox}^{bulk}\, D_{ox}^{1/2}}{\omega^{1/2}\, \cos\theta\, \left(4RT \cosh^2(\not{j}/2)\right)} \qquad (18)$$

Comparison of these expressions with the analogous expressions
for the alternating current reveals that the alternating reflectance
is phase-shifted 90° from the faradaic current. Thus the phase angle
ϕ is readily accessible. Also, it will be noted that while the
alternating current increases with the square root of the frequency, the
reflectance decreases.

Since it is desirable to obtain measurements at relatively high
frequencies, the measurement of reflectance may appear to be
disadvantageous with respect to measurement of the current. However,
as will be illustrated later, the current associated with charging
of the double layer capacitance does not, in general, contribute
to the spectral response. When the current is measured the contribution
from charging of the double layer capacitance increases, in the absence
of uncompensated resistance, linearly with the frequency. The ratio
of faradaic to background current thus also decreases as $\omega^{1/2}$ increases.
The absence of charging current in the spectral response implies that
the smaller signals obtained at higher frequencies may not be as
serious a problem as might first be expected.

The ratio of the magnitude of the fundamental harmonic current
to the corresponding reflectance parameter is given by

$$\frac{|I(\omega t)|}{|R(\omega t)|} = \frac{nFA \cos\theta}{4.606 \, \Delta E}$$

This relation may prove to be of value in the determination of extinction coefficients or n-values. More importantly, however, it shows that at any given frequency, the alternating reflectance is just a multiple of the corresponding alternating current. Hence all previously derived qualitative and quantitative aspects of the AC voltammetric response (eg. peak width at half-height, peak separation and cross-over potential in cyclic AC voltammetry) apply equally well to the SMACRS experiment.

In general, three approaches are possible for the extraction of heterogeneous kinetic parameters from AC voltammetric data and hence from alternating reflectance data. A computer fit of $R(\omega t)$ vs. $\omega^{\frac{1}{2}}$ may be used to evaluate the various paramters in equation (17)[15]. The peak separation as a function of sweep rate may be used in conjunction with working curves for the determination of the heterogeneous rate constant k_s , as in cyclic AC voltammetry[13]. The frequency dependence of the phase angle, ϕ , may be used to evaluate k_s and α , the charge transfer coefficient[11]. For several reasons, we have concentrated our efforts on the measurement of phase angles for the determination of heterogeneous kinetics. First, they are readily accessible to PSD techniques. In addition, they do not require the computation of working curves for the determination of heterogeneous rate constants. Most importantly,

Smith has shown[11] that phase angle data is not significantly affected by the magnitude of the modulation voltage, ΔE , for values up to 20 mV, provided $k_s > 10^{-2} \frac{cm}{s}$. The ability to use larger modulations can be particularly important in spectroelectrochemical studies where $\Delta \epsilon$ is small.

The various phase relations between the SMACRS response, the components of the alternating current, and the applied modulation voltage are most simply discussed in terms of a phasor diagram, as in Figure 1(a). Here, the applicability of the Randles equivalent circuit[16] (Figure 1(b)) is assumed. The applied voltage is represented by the phasor $\overrightarrow{\Delta E_{app}}$. $\overrightarrow{I_f}$, $\overrightarrow{I_c}$, and $\overrightarrow{I_t} = \overrightarrow{I_f} + \overrightarrow{I_c}$ represent the faradaic, capacitive, and total currents respectively. Note that in the presence of uncompensated resistance, R_u , the actual voltage across the interphase is given by $\Delta E_{eff} = \Delta E_{app} - I_t R_u$, and is thus phase-shifted through some angle, φ_c , from the applied modulation.

The phase angle, φ_s , between the faradaic current and the applied modulation is readily obtainable through phase sensitive detection of the in-phase and quadrature components of the SMACRS response, $\mathcal{R}'$ and $\mathcal{R}''$ respectively, since $\cot \varphi_s = \mathcal{R}'' / \mathcal{R}'$. If conditions of 100% iR compensation exist, then no further measurements are necessary since $\phi = \varphi_s$. This is most often, however, not the case. The phase angle between $\overrightarrow{I_f}$ and $\overrightarrow{\Delta E_{eff}}$ must then be determined from $\phi = \varphi_s + \varphi_c$. The phase angle φ_c can be determined if the magnitude of the total current, I_t , and its phase angle, φ_m , with respect to $\overrightarrow{\Delta E_{app}}$ are known in conjunction with R_u . In this case,

Smith has given[11]

$$\sin \varphi_c = \frac{I_t \, R_u \, \sin \varphi_m}{\left(\Delta E_{app}^2 + (I_t R_u)^2 - 2 \Delta E_{app} \, I_t \, R_u \cos \varphi_m \right)^{\frac{1}{2}}} \tag{20}$$

The phasor $\vec{I_t}$ is readily determined through phase sensitive detection of its in-phase and quadrature components, I_t' and I_t'' respectively, since $I_t = \left(I_t'^2 + I_t''^2 \right)^{\frac{1}{2}}$ and $\varphi_m = \tan^{-1}(I_t''/I_t')$. The value of R_u can be ascertained by similar measurements in a potential region where no faradaic process occurs. In this case an electrochemical cell may be represented by a resistor, R_u, and capacitor, C_{DL}, in series, and it is easily shown that $R_u = \frac{\Delta E_{app}}{I_t}\left(\frac{1}{1 + \tan^2 \varphi_m} \right)^{\frac{1}{2}}$.

The determination of the phase angle, ϕ, allows characterization of the heterogeneous kinetics through already well established relationships[11]. In particular, a plot of $\cot \phi$ vs. E_{DC} will exhibit a maximum at

$$E_{DC, \cot \phi_{max}} = E_{\frac{1}{2}}^r + \frac{RT}{n \mathcal{F}} \ln \frac{\alpha}{1 - \alpha} \tag{21}$$

and the charge transfer coefficient, α, is obtainable provided , the reversible half-wave potential is known. If measurements are made at the half-wave potential of the redox couple then

$$\cot \phi = 1 + (\omega D/2)^{\frac{1}{2}}/k_s$$

A plot of $\cot \phi$ vs. $\omega^{\frac{1}{2}}$ in conjunction with knowledge of the diffusion coefficient, D, then allows calculation of the standard heterogeneous rate constant, k_s.

RESULTS AND DISCUSSION

The PSD output obtained in a typical SMACRS experiment for the oxidation of ferrocyanide at a platinum electrode in aqueous KCl is illustrated in Figure 2. At low sweep rates (Figure 2(a)) the forward and reverse scans superimpose. The peak occurs at +.219 Volts vs. S.C.E. and coincides with the reversible half-wave potential, as estimated from cyclic voltammetry in the same electrochemical cell. This potential is invariant with frequency. The width of the peak at half-height is 94 mV, in good agreement with the theoretical value of 90mV expected[11] for the analogous AC response for a reversible 1-electron system.

At higher sweep rates, the forward and reverse scans are observed to separate, as predicted under cyclic AC voltammetric theory[13]. The point at which the forward and reverse scans coincide occurs at the same potential as the peak obtained under low scan rate conditions. Since the cross-over point has been shown[13] to occur at the same potential as that of maximum phase angle (ie. $E_{co} = E_{DC, cot \phi_{max}}$), the charge transfer coefficient, α , may be calculated as .5 from equation 21. This value may also be assumed from the invariance of the low scan rate peak potential with frequency, as it has been previously shown[11] that the peak potential reaches a limiting value of

$$E_p = E_{\frac{1}{2}}^R + \frac{RT}{n \mathcal{F}} \ell_n \frac{1-\alpha}{\alpha}$$

as frequency increases.

It will be noted that the base lines of Figure (2) are flat and correspond to electrical zero. This is in contrast to the non-zero curved base lines arising from charging current contribution to the responses generally obtained with conventional AC voltammetric methods (see, for example, reference 17).

A plot of $\cot\phi$ (lower trace) vs. $\omega^{\frac{1}{2}}$ obtained from SMACRS data on the ferro-ferricyanide system is illustrated in Figure (3). The upper trace corresponds to values of $\cot\varphi_s$ obtained before correction for the effects of uncompensated resistance, as discussed above. From the $\cot\phi$ data, we have calculated a standard rate constant $k_s = .096 + .008$ cm s^{-1}, assuming a diffusion coefficient $D = 6.32$ X 10^{-6} cm^2 s^{-1} (18). This is in good agreement with the value $.090 + .009$ cm s^{-1} we obtained with $\cot\phi$ data from conventional AC methods at the same electrode, and with the literature value[19] of .09 obtained under the same conditions.

The value of R_u used in equation (20) to calculate the $\cot\phi$ data of Figure 3 was only 2.3 ohms. It is apparent that, even with this small uncompensated resistance, the magnitude of the phase angle correction, φ_c, is large, particularly at higher frequencies. This is largely due to greater currents resulting from the use of 10mM concentrations and 18 mV modulation voltages. These conditions were desirable in this case because of the small value of $\Delta\epsilon$ associated with the ferro-ferricyanide system ($\Delta\epsilon = 1020$ at 420 nm)[14]. For many systems of interest, however, $\Delta\epsilon$ will be larger than this,

and concentrations and modulation voltages may be reduced accordingly.
For the reduction of manganese-porphyrin complexes in DMSO[20] ($\Delta\epsilon \cong 8 \times 10^4$),
for instance, good signal to noise ratios have been obtained in
10^{-5} M solutions with $\Delta E = 8$ mV. A further reduction in current
should be obtainable through the use of smaller electrodes than we have
used in this study (7mm diameter). Under conditions of minimal
current, in conjunction with positive feedback iR compensation, the
importance of the phase angle correction may be minimized.

The particularly wide range of heterogeneous rate constants
accessible to conventional AC techniques (10^{-5} to 1 cm s^{-1})[10] should
be equally available through the methodology discussed here. Although
we have discussed only the simple quasi-reversible mechanism, the
method should be readily extendable to include other cases, including
those involving coupled homogeneous reactions, for which AC theory has
already been developed. The selectivity attainable through the
combined use of spectroscopic observation with small applied potential
perturbations should make the technique particularly useful in the
delineation of overlapping voltammetric waves, and in the qualitative
diagnosis of complicated reaction schemes. We feel, in addition, that
the inherently greater sensitivity associated with reflectance
measurements in conjunction with the convenient data format and
selectivity obtained make SMACRS more attractive for purposes of analysis
than any other currently available spectroelectrochemical technique.

EXPERIMENTAL

A standard MSRS linear diffusion cell (Figure 4) was used in these experiments. The working electrode was a 7mm diameter polished platinum disk heat shrunk into the end of a 9 mm o.d. Kel-F tube. A variable amplitude sinusoidal voltage from a Global Associates function generator was added to a variable sweep rate potential ramp from a HiTek PPR1 waveform generator at the adder input of a HiTek DT2102 potentiostat (Figure 5). Light from a 200W Hg-Xe lamp was focused onto the electrode surface (45 angle of incidence) after being passed through a GCA MacPherson 201 monochromator. The reflected light was collected by a quartz focusing lens and directed to an RCA 31000M photomultiplier tube (PMT). The PMT was operated in a constant current feedback mode so that $\frac{\Delta \mathcal{R}}{\mathcal{R}}$ was measured directly. A PAR model HR-8 and a Bentham 223 lock-in amplifier were used for the simultaneous measurement of I_t and $\mathcal{R}(\omega t)$. The phase sensitive detector reference waveform was taken directly between the reference electrode (isolated by a high input impedence voltage follower located at the reference electrode) and the working electrode. Outputs from the lock-in amplifiers were recorded on a Hewlett Packard 7045A recorder.

Reagent grade potassium ferrocyanide and potassium chloride were used. Solutions were prepared in triply distilled water.

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CAPTIONS FOR FIGURES

1. Figure 1. (a) Phase relations in the SMACRS experiment, notation as defined in the text (b) The Randles Equivalent circuit, R_{ct} = charge transfer resistance, W = Warburg impedance, other notation as defined in text.

2. Figure 2. SMACRS for oxidation of 10mM $K_4Fe(CN)_6$ in 1M aq. KCl, wavelength observed = 420nm (a) $\omega/2\pi$ = 43.9 Hz, ν = 2 mV/s (b) $\omega/2\pi$ = 75.0 Hz, ν = 200 mV/s.

3. Figure 3. Cot ϕ vs. $\omega^{\frac{1}{2}}$ for oxidation of 10mM $K_4Fe(CN)_6$ in 1M aq. KCl. Squares represent cot ϕ_s , circles represent calculated cotϕ ; E_{DC} = .219 V vs. SCE, ΔE = 18 mV.

4. Figure 4. Optical cell configuration for MSRS and SMACRS.

5. Figure 5. Instrumentation for SMACRS: A, Power supply for light source; B, light source; C, monochromator; D, electrochemical cell; E, potentiostat; F, waveform generator; G, oscillator; H, photomultiplier; I, current follower; J, integrator; K, PMT hi-voltage source; L, lock-in amplifier; M, Recorder.
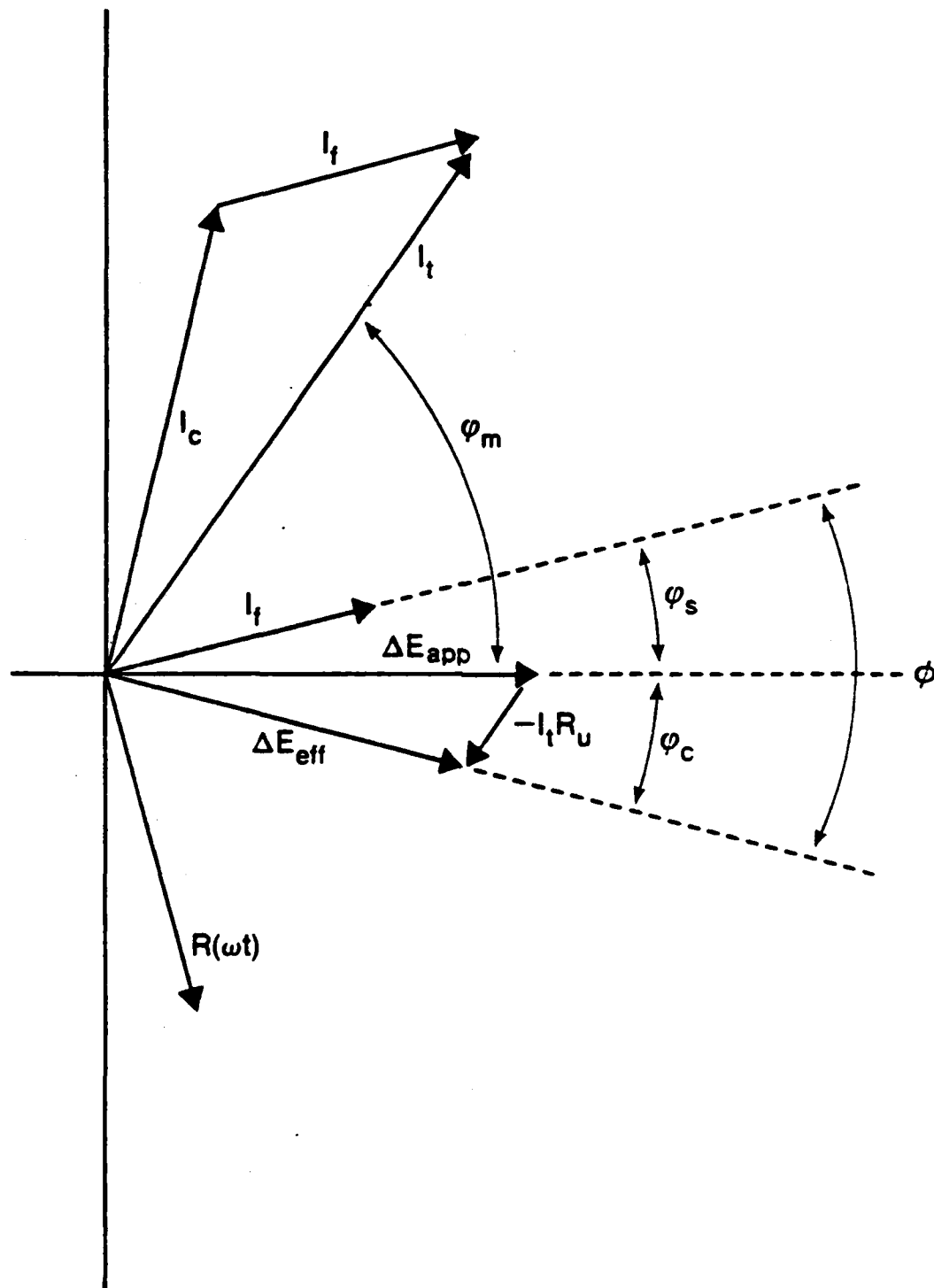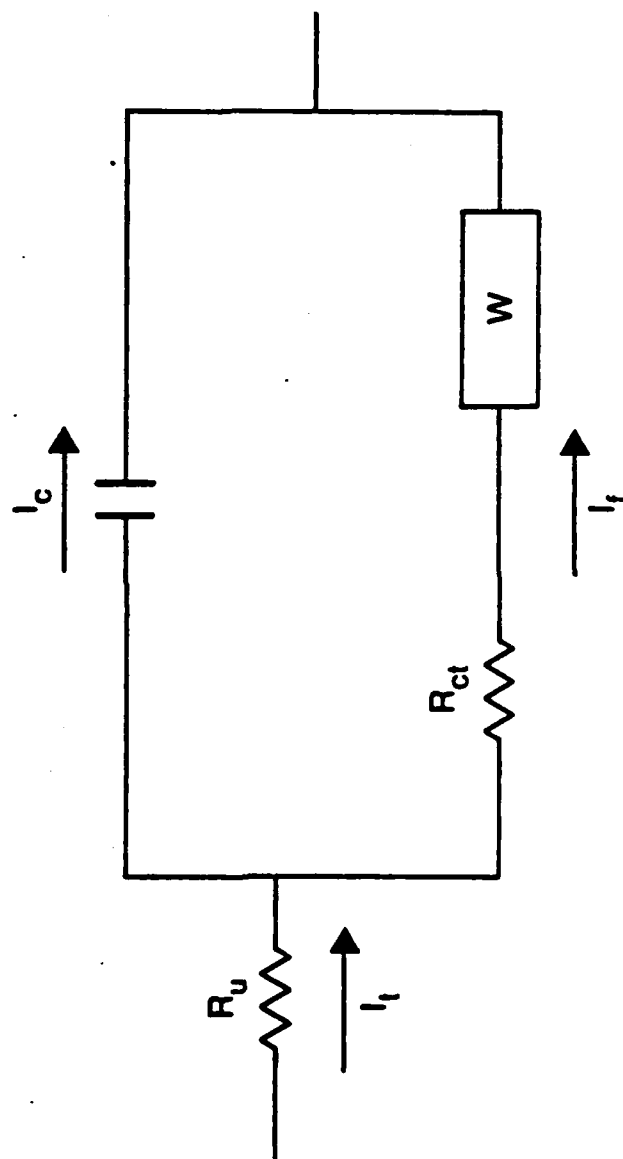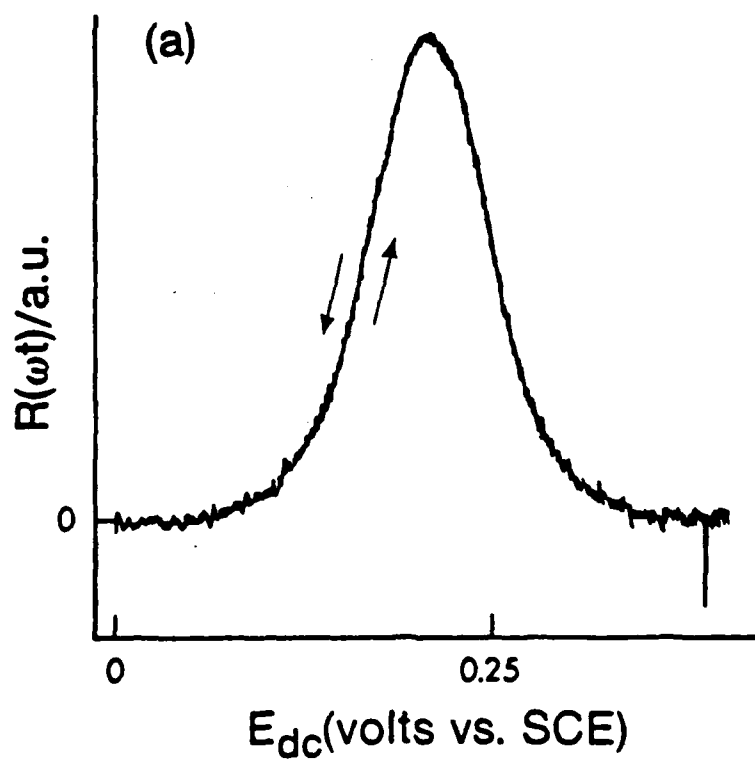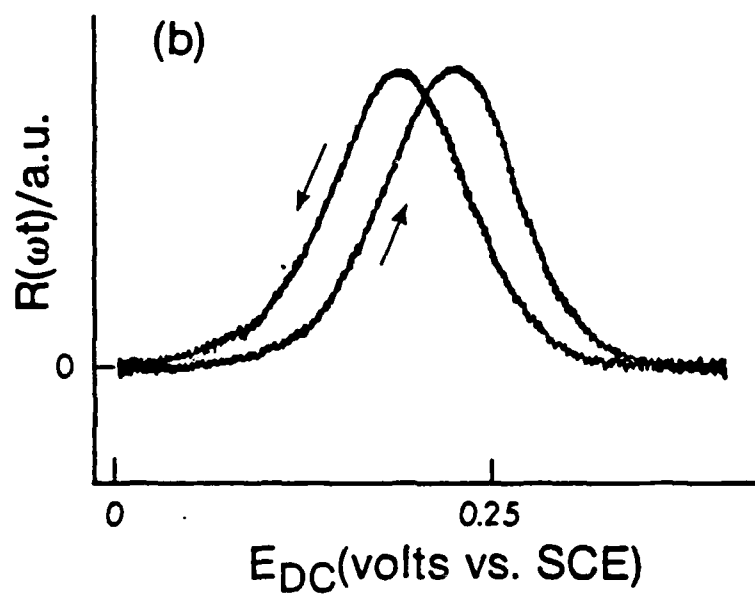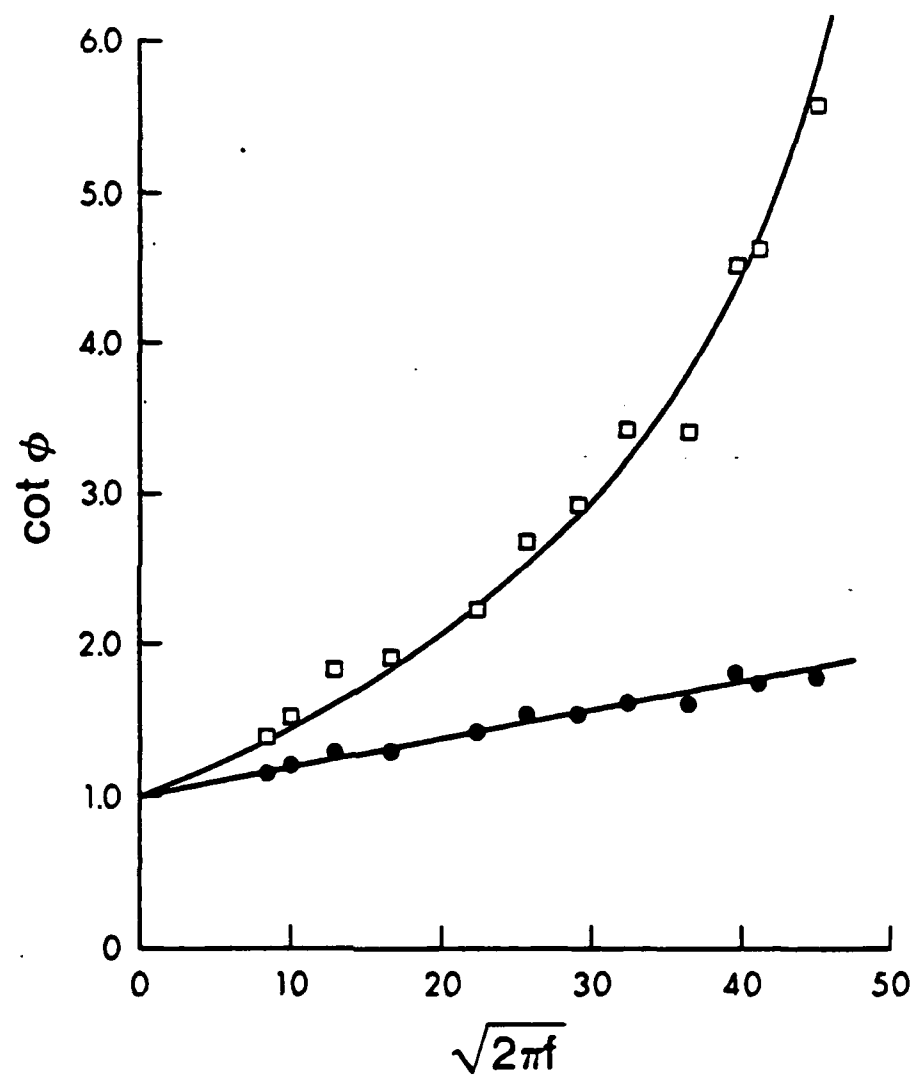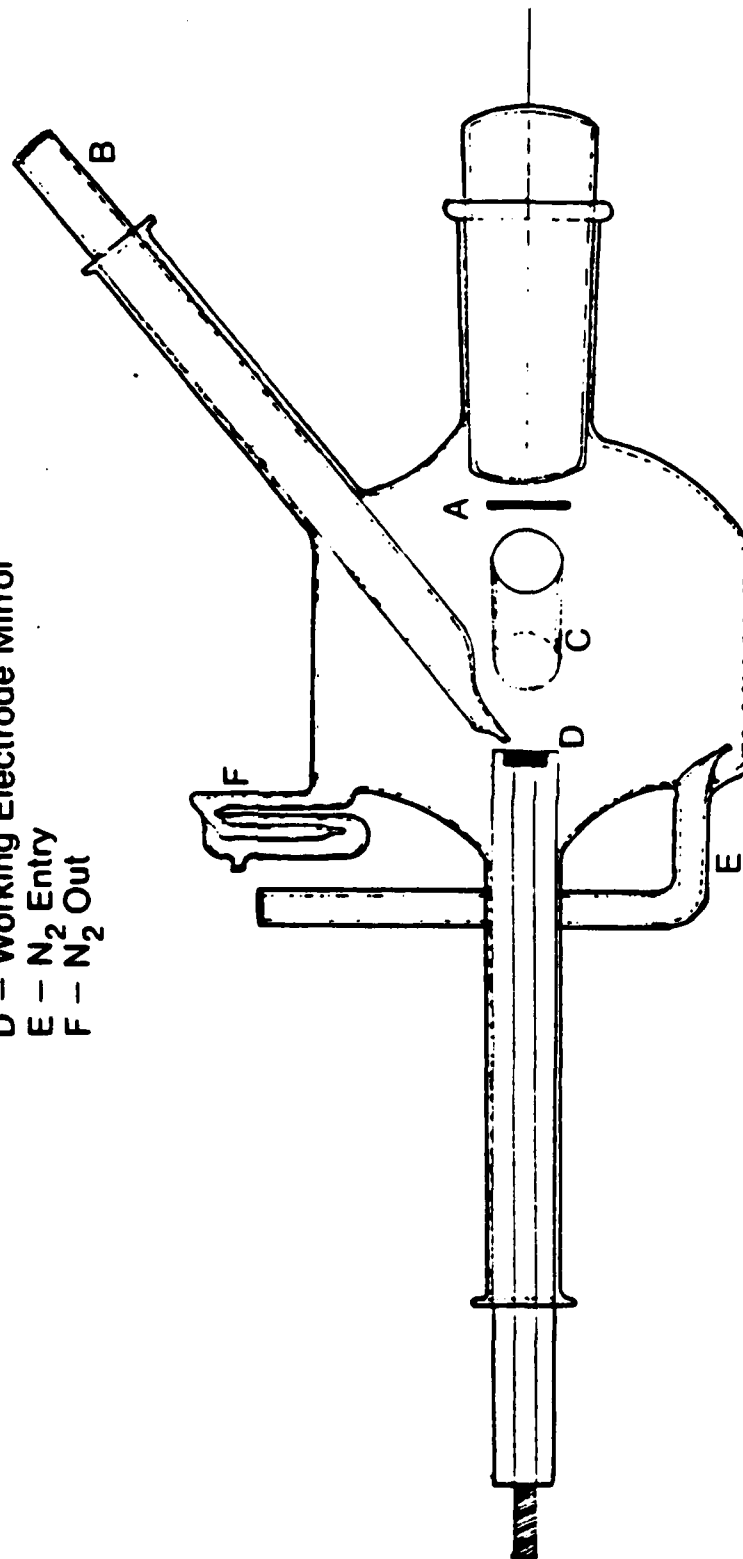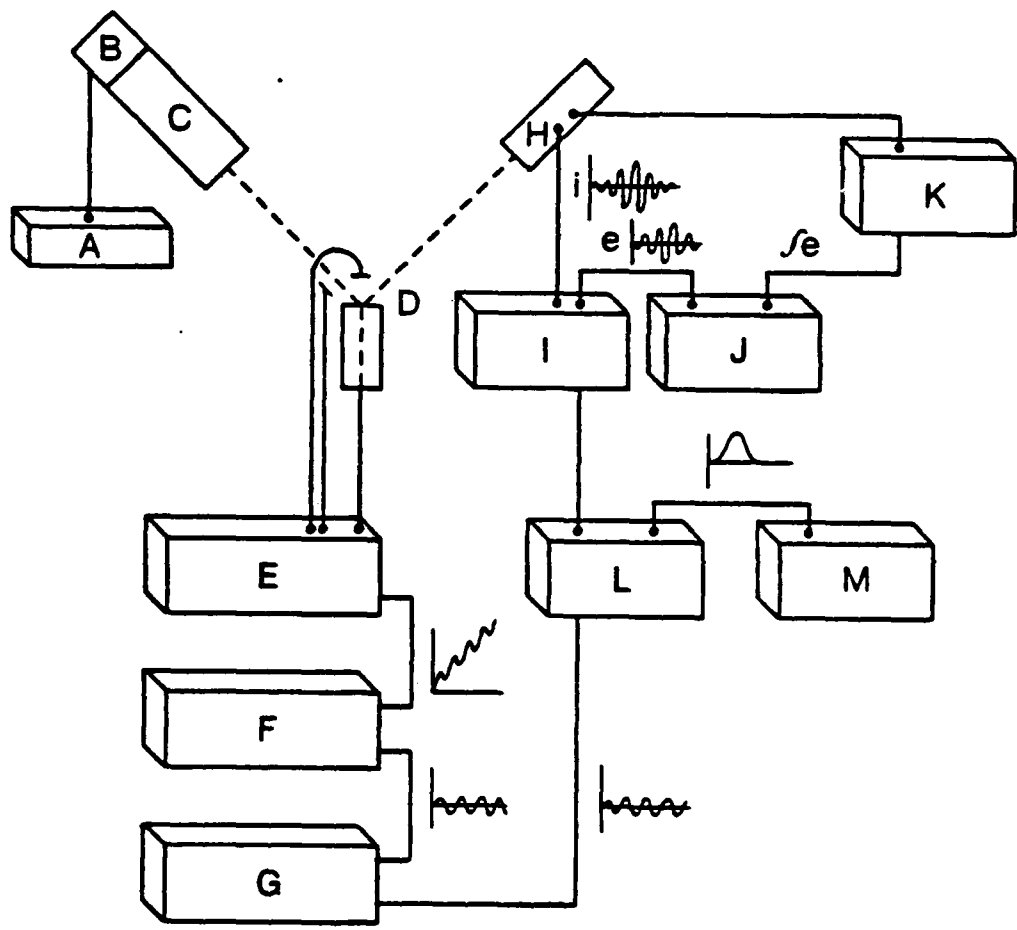
A – Secondary Electrode
B – Reference Electrode
C – Light Entry (Exit) Port
D – Working Electrode Mirror
E – N_2 Entry
F – N_2 Out